



CoFC

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Marta DREWNIAK et al.

Confirmation No.: 3423

Patent No.: 6,770,697 B2

Application No.: 10/072,536

Patent Date: August 3, 2004

Filing Date: February 7, 2002

For: HIGH MELT-STRENGTH
POLYOLEFIN COMPOSITES AND
METHODS FOR MAKING AND
USING SAME

Attorney Docket No.: 86006-6400

REQUEST FOR CERTIFICATE OF CORRECTION UNDER 37 C.F.R. § 1.322

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Certificate
AUG 23 2004
of Correction

Sir:

Patentees hereby respectfully request the issuance of a Certificate of Correction in connection with the above-identified patent. The corrections are listed on the attached Form PTO-1050, submitted in duplicate. The corrections requested are as follows:

Title page at Item (56). References Cited:

U.S. PATENT DOCUMENTS, after "6,380,295 B1 04/2002 Ross et al.
524/443", insert -- 6,407,155 B1 3/2000 Qian et al. 524/445 --.

FOREIGN PATENT DOCUMENTS, after "JP 51075761 A 3/1976",
insert -- WO WO 99/47598 3/1999 --.

Support for the above corrections can be found on the Third Party Submission in Published Applications filed December 18, 2002.

OTHER PUBLICATIONS: Galgali reference, change "Galgali, O., et al." to
-- Galgali, G., et al. --. See Applicants Third Information Disclosure Statement filed
December 8, 2003 in support thereof.

Column 22:

Line 57 (claim 15, last line), before "organically modified clay" delete "or". See
Applicants' Amendment filed December 8, 2003 in support thereof.

AUG 24 2004

The requested corrections are for errors that appear to have been made by the Office. Therefore, no fee is believed to be due for this request. Should any fees be required, however, please charge such fees to Winston & Strawn LLP Deposit Account No. 50-1814. Please issue a Certificate of Correction in due course.

Respectfully submitted,

8/18/04
Date

Jeffrey A. Wolfson
Jeffrey A. Wolfson (Reg. No. 42,234)

WINSTON & STRAWN LLP
Customer No. 28765

202-371-5904

**UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION**

PATENT NO.: 6,770,697 B2
DATED: August 3, 2004
INVENTORS: Drewniak et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title Page, Item (56), References Cited:

U.S. PATENT DOCUMENTS, after "6,380,295 B1 04/2002 Ross et al. 524/443",
insert -- 6,407,155 B1 3/2000 Qian et al. 524/445 --.

FOREIGN PATENT DOCUMENTS, after "JP 51075761 A 3/1976",
insert -- WO WO 99/47598 3/1999 --.

OTHER PUBLICATIONS: Galgali reference, change "Galgali, O., et al." to
-- Galgali, G., et al. --.

Column 22:

Line 57, before "organically modified clay", delete "or".

**UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION**

PATENT NO.: 6,770,697 B2
DATED: August 3, 2004
INVENTORS: Drewniak et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title Page. Item (56). References Cited:

U.S. PATENT DOCUMENTS, after "6,380,295 B1 04/2002 Ross et al. 524/443",
insert -- 6,407,155 B1 3/2000 Qian et al. 524/445 --.

FOREIGN PATENT DOCUMENTS, after "JP 51075761 A 3/1976",
insert -- WO WO 99/47598 3/1999 --.

OTHER PUBLICATIONS: Galgali reference, change "Galgali, O., et al." to
-- Galgali, G., et al. --.

Column 22:

Line 57, before "organically modified clay", delete "or".



US006770697B2

(12) **United States Patent**
Drewniak et al.

(10) Patent No.: **US 6,770,697 B2**
(45) Date of Patent: **Aug. 3, 2004**

(54) **HIGH MELT-STRENGTH POLYOLEFIN COMPOSITES AND METHODS FOR MAKING AND USING SAME**

(75) Inventors: **Marta Drewniak**, Carrollton, TX (US);
Xia Zhao, Garfield, NJ (US); **Satchit Srinivasan**, Carrollton, TX (US)

(73) Assignee: **Solvay Engineered Polymers**, Grand Prairie, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 154 days.

(21) Appl. No.: **10/072,536**

(22) Filed: **Feb. 7, 2002**

(65) **Prior Publication Data**

US 2002/0156171 A1 Oct. 24, 2002

Related U.S. Application Data

(60) Provisional application No. 60/269,386, filed on Feb. 20, 2001.

(51) Int. Cl.⁷ **C08K 3/34**

(52) U.S. Cl. **524/445**; 524/321; 524/425;
524/538; 523/351; 525/70; 264/41; 264/349;
264/540

(58) Field of Search 524/445, 321,
524/538, 425; 523/351; 525/70; 264/540,
349, 41

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,810,734 A * 3/1989 Kawasumi et al. 523/216
5,164,460 A 11/1992 Yano et al. 524/445
5,552,469 A 9/1996 Beall et al. 524/445

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

EP 0 807 659 B1 11/1999

EP 1 055 706 A1 11/2000
JP 51075761 A 3/1976
WO WO 00/12572 3/2000
WO WO 01/30864 A2 5/2001
WO WO 01/48080 A1 7/2001
WO WO 02/066553 A2 8/2002

WO 99/47598 3/1999

OTHER PUBLICATIONS

Kato, M.; Usuki, A.; Okada, A., "Synthesis of Polypropylene Oligomer-Clay Intercalation Compounds," *Journal of Applied Polymer Science*, vol. 66, pp. 1781-1785, 1997.

Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; and Okada, A., "Preparation and Mechanical Properties of Polypropylene-Clay Hybrids," *Macromolecules*, vol. 30, No. 20, pp. 6333-6338, Aug. 1997.

Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A., "Preparation and Mechanical Properties of Polypropylene-Clay Hybrids Using a Maleic Anhydride-Modified Polypropylene Oligomer," *Journal of Applied Polymer Science*, vol. 67, pp. 87-92, 1998.

Lau, H.C.; Bhattacharya, S.N.; Field, G.J., "Melt Strength of Polypropylene: Its Relevance to Thermoforming," *Polymer Engineering and Science*, vol. 38, No. 11, Nov. 1998.

(List continued on next page.)

Primary Examiner—David W. Wu

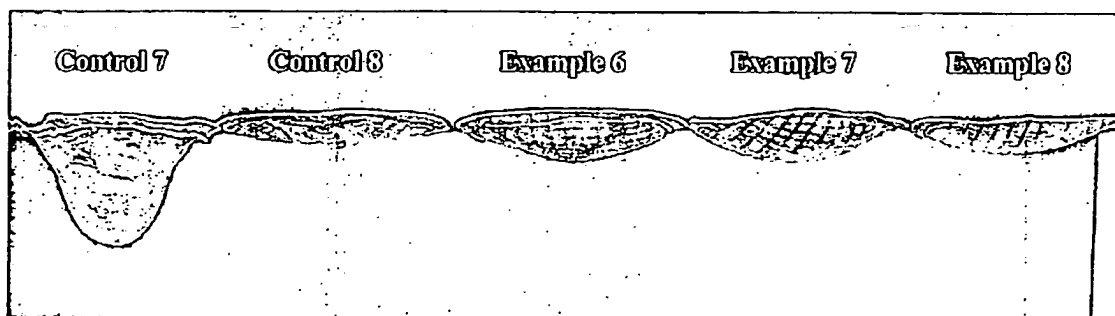
Assistant Examiner—Henry S Hu

(74) Attorney, Agent, or Firm—Winston & Strawn LLP

(57) **ABSTRACT**

The invention includes a process for preparing an improved melt-strength polyolefin blend by incorporating a polyolefin/clay nanocomposite product. The nanocomposite-modified polyolefin blend is used to form articles through processing operations that involve stretching and/or drawing, such as thermoforming, melt spinning, blow molding and foaming. The addition of the nanocomposite product to the polyolefin blend improves the sag resistance of the polyolefin and broadens the processing window of the operation.

22 Claims, 5 Drawing Sheets



U.S. PATENT DOCUMENTS

5,759,938 A	6/1998	Cody et al.	502/62
5,853,886 A	12/1998	Pinnavaia et al.	428/403
5,910,523 A	6/1999	Hudson	523/213
5,973,053 A *	10/1999	Usuki et al.	524/445
5,985,971 A	11/1999	Srinivasan et al.	524/425
6,036,765 A	3/2000	Farrow et al.	106/487
6,051,643 A	4/2000	Hasegawa et al.	524/445
6,103,817 A	8/2000	Usuki et al.	524/574
6,117,541 A	9/2000	Frisk	428/327
6,117,932 A	9/2000	Hasegawa et al.	524/445
6,121,361 A	9/2000	Usuki et al.	524/445
6,136,908 A	10/2000	Liao et al.	524/445
6,153,680 A *	11/2000	Shah et al.	524/425
6,225,394 B1	5/2001	Lan et al.	524/445
6,337,046 B1 *	1/2002	Bagrodia et al.	264/540
6,380,295 B1	4/2002	Ross et al.	524/443
6,451,897 B1	9/2002	Niyogi	524/445
6,462,122 B1 *	10/2002	Qian et al.	524/445
6,583,209 B2	6/2003	Mehta et al.	524/445
2002/0161096 A1	10/2002	Loontjens et al.	524/445

OTHER PUBLICATIONS

Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Kato, M.; Tsukigase, A.; Usuki, A., "Polyolefin-clay hybrids based on modified polyolefins and organophilic clay," *Macromolecular Materials and Engineering*, vols. 280/281, pp. 76-79, 2000.

Alexandre, M.; Dubois, P., "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," *Materials Science and Engineering*, vol. 28, pp. 1-63, 2000.

G.

Galgali, O. et al., "A Rheological Study on the Kinetics of Hybrid Formation in Polypropylene Nanocomposites," *Macromolecules*, vol. 34, pp. 852-858 (2001).

Kim, K-N, et al., "Mixing Characteristics and Mechanical Properties of Polypropylene-Clay Composites," *ANTEC 2000*, vol. 3, pp. 3782-3786 (2000).

Kodgire, P., et al., "PP/Clay Nanocomposites: Effect of Clay Treatment on Morphology and Dynamic Mechanical Properties," *J. Applied Science*, vol. 81, pp. 1786-1792 (2001).

Kurokawa, Y., et al., "Structure and Properties of a Montmorillonite/Polypropylene Nanocomposite," *J. Materials Science Letters*, vol. 16, pp. 1670-1672 (1997).

Oya, A., "Polypropylene-Clay Nanocomposites," *Wiley Series in Polymer Science*, John Wiley & Sons, Ltd., Chapter 8, pp. 152-172 (2000).

Oya, A., et al., "Factors Controlling Mechanical Properties of a Clay Mineral/Polypropylene Nanocomposite," *J. Materials Science*, vol. 35, pp. 1045-1050 (2000).

Reichert, P., et al., "Poly(propylene)/Organoclay Nanocomposite Formation: Influence of Compatibilizer Functionality and Organoclay Modification," *Macromol. Mater. Eng.*, vol. 275, pp. 8-17 (2000).

Solomon, M.J., et al., "Rheology of Polypropylene/Clay Hybrid Materials," *Macromolecules*, vol. 34, pp. 1864-1872 (2001).

Svoboda, P., et al.: "Structure and Mechanical Properties of Polypropylene and Polystyrene/Organoclay Nanocomposites," Department of Chemical Engineering, The Ohio State University, Jun. 25-27, 2001.

* cited by examiner-

6,407,155 B1 3/2000 Qian et al. 524/445

modified melt strength to the melt strength before modification measured at 220° C. is at least about 1.6 but no more than about 14 and the final polyolefin blend has a shear viscosity that is at least about 5 times that of the shear viscosity of the polymer blend measured under the same conditions but without the organically modified clay.

4. A method of manufacturing an article which comprises a polyolefin/clay nanocomposite blend comprising:

combining from about 50 to 98 percent by weight of a polyolefin comprising a non-functionalized homopolymer or copolymer of propylene, and either (a) copolymer of ethylene and an alpha-olefin with an optional diene; or (b) a styrene copolymer of ethylene or propylene; or a mixture thereof, from about 1 to 20 percent by weight of a functionalized polyolefin, and an organically modified clay in an amount sufficient to provide a modified melt strength, so that a ratio of the modified melt strength of the final polyolefin blend to the melt strength of the polyolefin blend before modification with the organically modified clay measured at 220° C. is at least about 1.5 but no more than about 15; and

forming the article using the polyolefin/clay nanocomposite blend.

5. The method of claim 4, wherein the polyolefin blend in the article comprises from about 70 to 95 percent by weight of polyolefin, from about 1 to 10 percent by weight of functionalized polyolefin, and from about 4 to 20 percent by weight of organically modified clay to provide a ratio of the melt strength of the modified blend to the melt strength of the blend before modification measured at 220° C. of at least about 1.6 but no more than about 14.

6. The method of claim 4, wherein the polyolefin blend in the article comprises from about 85 to 92 percent by weight of polyolefin, from about 2 to 5 percent by weight of functionalized polyolefin, and from about 6 to 10 percent by weight of organically modified clay to provide a ratio of the melt strength of the modified blend to the melt strength of the blend before modification measured at 220° C. of at least about 1.6 but no more than about 14.

7. The method of claim 1 wherein the forming comprises at least one of thermoforming, extrusion, melt spinning, blow molding or foam processing.

8. An article formed from a final polyolefin blend containing a polyolefin/clay nanocomposite masterbatch comprising:

from about 0 to 99 percent by weight of polyolefin from about 1 to 100 percent by weight of a functionalized polyolefin, and from about 10 to 50 percent by weight of an organically modified clay, and any optional additive components,

wherein the final polyolefin blend comprises from about 1 to 30 percent by weight of the nanocomposite masterbatch and about 70 to 99 percent by weight of a polyolefin blend comprising a non-functionalized homopolymer or copolymer of propylene, and either (a) copolymer of ethylene and an alpha-olefin with an optional diene; or (b) a styrene copolymer of ethylene or propylene; or a mixture thereof, and

wherein the organoclay is sufficiently exfoliated into the polyolefin blend to provide the final polyolefin blend with a modified melt strength so that the ratio of the modified melt strength of the final polyolefin blend to the melt strength of the polyolefin blend before modification with the organically modified clay measured at 220° C. is at least about 1.5 but no more than about 15.

9. The article of claim 8, wherein the masterbatch is present in an amount from about 2 to 27 percent by weight

and comprises from about 50 to 80 percent by weight of polyolefin, from about 20 to 50 percent by weight of functionalized polyolefin, and from about 20 to 48 percent by weight of organically modified clay, and the polyolefin blend is present in an amount from about 73 to 98 percent by weight, to form the final polymer blend which has a modified melt strength so that the ratio of the modified melt strength to the melt strength before modification measured at 220° C. is at least about 1.5 but no more than about 15.

10. The article of claim 8, wherein the masterbatch is present in an amount from about 3 to 25 percent by weight and comprises from about 60 to 70 percent by weight of polyolefin, from about 30 to 40 percent by weight of functionalized polyolefin, and from about 30 to 45 percent by weight of organically modified clay, and the polyolefin blend is present in an amount from about 75 to 97 percent by weight, to form the final polyolefin blend which has a modified melt strength so that the ratio of the modified melt strength to the melt strength before modification measured at 220° C. is at least about 1.6 but no more than about 14 and the final polyolefin blend has a shear viscosity that is at least about 5 times that of the shear viscosity of the polymer blend measured under the same conditions but without the organically modified clay.

11. The article of claim 8, wherein the functionalized polyolefin comprises a homopolymer or copolymer of propylene, a homopolymer or copolymer of ethylene, or a mixture thereof, wherein a functional monomer with a pendant reactive polar group is grafted onto the polyolefin.

12. The article of claim 8, wherein the nanocomposite-modified polyolefin blend further comprises one or more optional additive components including nucleating agents, fillers, plasticizers, impact modifiers, colorants, mold release agents, lubricants, antistatic agents, pigments, fire retardants, and ultraviolet stabilizers, or mixtures thereof, and the alpha-olefin comprises octene.

13. The article of claim 8, wherein the addition of the nanocomposite masterbatch provides a range of temperatures for forming the article that is at least about 10° C. greater than without the inclusion of a sufficient amount of the clay nanocomposite.

14. An automotive component, a building material, a packaging material, an electrical material, or a nonwoven fabric or fiber comprising the article of claim 8.

15. An article formed from a modified polyolefin blend comprising from about 50 to 98 percent by weight of polyolefin comprising a non-functionalized homopolymer or copolymer of propylene, and either (a) copolymer of ethylene and an alpha-olefin with an optional diene; or (b) a styrene copolymer of ethylene or propylene; or a mixture thereof, from about 1 to 20 percent by weight of functionalized polyolefin, and from about 1 to 30 percent by weight of organically modified clay that is sufficiently dispersed in the polyolefin and functionalized polyolefin to provide a modified melt strength of the final polyolefin blend that is greater than the melt strength of the polyolefin blend before modification with the organically modified clay.

16. The article of claim 15, wherein the polyolefin blend comprises from about 70 to 95 percent by weight of polyolefin, from about 1 to 10 percent by weight of functionalized polyolefin, and from about 4 to 20 percent by weight of organically modified clay.

17. The article of claim 15, wherein the polyolefin blend comprises about 85 to 92 percent by weight of polyolefin, from about 2 to 5 percent by weight of functionalized polyolefin, and from about 6 to 10 percent by weight of organically modified clay.